PHASE CHANGES AND CHEMISTRY
AT HIGH PRESSURES AND TEMPERATURES

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PHASE CHANGES AND CHEMISTRY AT HIGH PRESSURES AND TEMPERATURES

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Some of the interesting changes that occur in nature involve phase changes and chemical reactions at high pressures and temperatures. This paper gives new equilibrium and nonequilibrium calculations on reactive mixtures and a review on recent theoretical works in this field.

1. INTRODUCTION

Shock wave and high explosive (HE) experiments have provided a significant amount of experimental data on reactive mixtures, covering pressures up to one hundred gigapascal and temperatures to a few electron volts. On the theoretical side, intermolecular potentials, computer simulations, equations of state (EOS) theories, and methods of handling chemical reactions are at a stage where a realistic calculation is possible to interpret experimental data.

For this purpose we have developed a statistical mechanical code (CHEQ) and used it to study several molecular systems[1] and HE's.[2,3] Although the assumption of thermodynamic equilibrium is satisfactory to explain a large body of experimental dynamic data, there are cases for which the equilibrium assumption alone is inadequate. Unfortunately, kinetic data under strong shock conditions are sparse and difficult to interpret. We analyze below the rate effects in both condensed carbon[4] and shocked liquid nitrogen.[5-7] Prior to this, we examine the extent to which the equilibrium assumption can explain experimental data.

2. THEORY

Shock wave experiments relate pressure (P) and volume (V) to energy (E) through the so-called Hugoniot,

$$E = E_0 + \frac{1}{2} (P + P_0)(V_0 - V), \qquad (1)$$

which is simply the law of energy conservation between the state (P_0, V_0, E_0) ahead and the state (P,V,E) behind the shock front. The P and E are evaluated from the Helmholtz free energy (A),

$$P = -(\partial A/\partial V)_T, \quad E = -[\partial(A/T)/\partial(1/T)]_V . \quad (2)$$

In computing A,[8] we use the exponential-six (exp-6) potential,

$$\phi(r) = \frac{\epsilon}{\alpha-6} \{6 \exp[\alpha(1-r/r^*)] - \alpha(r^*/r)^6\}, \quad (3)$$

where parameters α, ϵ, and r^* are known for many simple molecules.[3] By solving for a particular (P,V) point which satisfies Eq. (1), we obtain a theoretical Hugoniot.

For a mixture case, we use the improved van der Waals 1-fluid model.[9] It assumes that all molecules in mixtures are identical and interact with an effective exp-6 potential,

$$(r^\star)^3 = \sum x_i x_j (r^\star_{ij})^3,$$

$$\epsilon = \sum x_i x_j (r^\star_{ij})^3 \epsilon_{ij}/(r^\star)^3, \qquad (4)$$

$$\alpha = \sum x_i x_j (r^\star_{ij})^3 \epsilon_{ij} \alpha_{ij}/(r^\star)^3 \epsilon,$$

where x_i is the concentration of molecular species i.

The formulae described so far are sufficient if there is no chemical reaction or phase change. Otherwise, we need to minimize the Gibbs free energy (G=A+PV) with respect to x_i. CHEQ does this computational chore, using additional EOS expressions (if needed) for heterogeneous mixtures.

3. APPLICATIONS

Reaction $H_2 \rightarrow 2H$. Exp-6 potentials used in our calculations are: α=11.1, ϵ/k=36.4K, r*=3.43A for H_2-H_2 and α=13, ϵ/k=20K, r*=1.4A for H-H. The former set is based on shock and static data,[9,10] and the latter on an averaged repulsion of the ground and first excited states of H_2. The H-H_2 exp-6 parameters are obtained from

$$\alpha_{ij} = \sqrt{\alpha_{ii}\alpha_{jj}} \;,\; \epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \;,$$

$$r^\star_{ij} = \frac{1}{2}(r^\star_{ii} + r^\star_{jj}) \;, \qquad (5)$$

where i = H_2 and j=H.

The short-ranged H-H repulsion (1.4A) favors the dissociation of H_2 at high P. In Fig. 1, the dissociation occurs at high T's without a phase change. At low T's, however, the dissociation is a first-order phase change. The Hugoniot of liquid H_2 comes close to but stays outside the phase change region.

Interpretation of the computed results is facilitated by referring to the Gibbs phase rule, f=2+c-p (f = degrees of freedom, p = phases present, and c = the number of components). Since c=1, we have: (1) p=1 and f=2 - the dissociation occurs without phase change, and (2) p=2 and f=1 - the dissociation
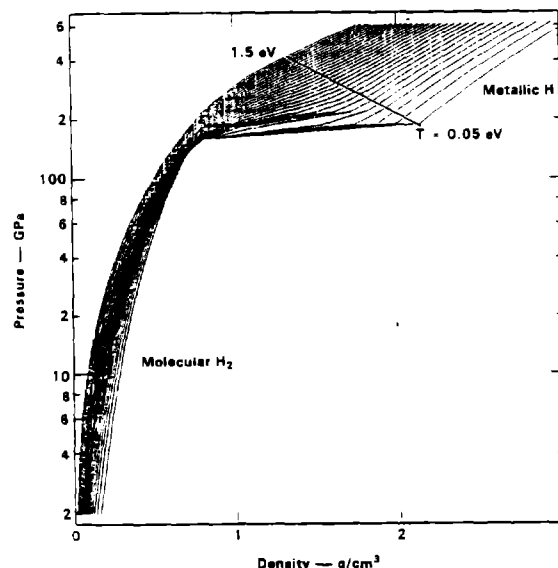

FIGURE 1
Isotherms of hydrogen in the dissociative ($H_2 \rightarrow H$) regime.

is a first (not a second or higher) order phase change. If (2) has a lower free energy than that of (1), it is the thermodynamically stable state. It in turn depends on H_2-H_2, H-H, and H-H_2 potentials. Among the three potentials the H-H interaction is least accurate. Because the one used in our calculation is too short-ranged, Fig. 1 shows an undesirably large density change across the transition. Our preliminary calculation is presented only to demonstrate the theoretical possibility of a first-order phase change in fluid phases.

Reaction $N_2 \rightarrow 2N$. Shocked liquid nitrogen exhibits both a shock-cooling and a softening of the shock pressure.[5,6] A theoretical Hugoniot in Fig. 2 is obtained using a reliable N_2-N_2 potential,[7,11] the N_2-N parameters from Eq.(5), and an adjustment of the N-N parameters (α=20, r*=2.5A, ϵ/k=20K) to fit the shock wave data above 30GPa. A short N-N repulsion (2.5A), as in the case of hydrogen, favors dissociation under shock compression.
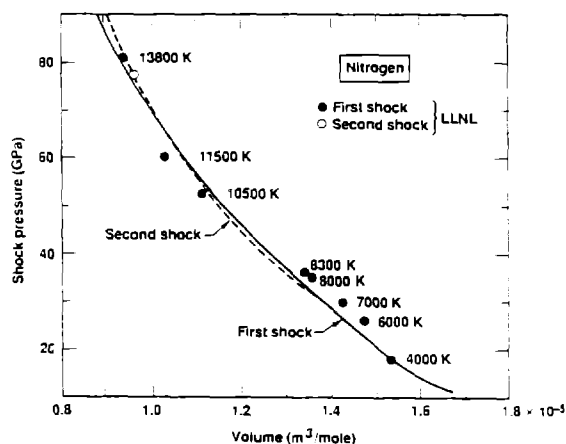
FIGURE 2
Hugoniots of liquid nitrogen: experiment[5]
(points) and theory (lines). Predicted shock
temperatures are included.

A three-dimensional view of isotherms (Fig.
3) shows that the dissociation occurs without
a phase change (p=1 and c=1), and that the
isotherms gently "dip" within the dissociation
region. When projected onto the P-V plane,
the isotherms appear to cross each other.
Calculations on shock temperatures and a
reflected shock path (Fig. 2) agree closely
with experiment, except within the
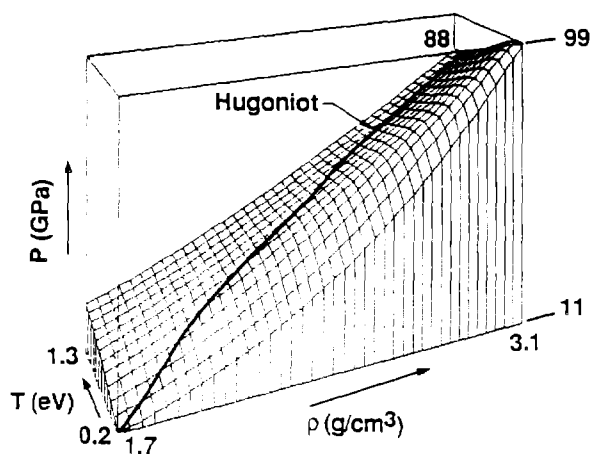dissociation region where the calculations

FIGURE 3
EOS surface and a Hugoniot of nitrogen.

give slightly higher temperatures. Although
the shock cooling is predicted along some
reflected paths, it occurs at a higher
pressure than the experimental value and its
extent is less. This may be due to kinetic
effects associated with the dissociation
process (discussed below). Efforts are under
way to refine the N-N parameters.[7]

We have estimated the dissociation barrier
of nitrogen.[12] Along the principal Hugoniot,
the computed barrier height, $\Delta F^{\neq}/kT$, is 9.3
at 20GPa (99.98 mole % N_2 dissociated) and 1.4
at 85GPa (56 mole % N_2 dissociated). The
estimated time scales for dissociation are
5000ns at 20GPa and 1.23ns at 85GPa. The
former is too long compared to the time scale
(order of 100ns) of the shock experiments.
But, since dissociated atoms are few in
number, thermodynamic properties are
essentially those of the undissociated
system. Both time scales will cross each
other at approximately 20GPa. The
aforementioned differences in the measured and
computed temperatures and an apparent
"shoulder" in the experimental Hugoniot may be
a manifestation of this rate effect, as seen
below in shock data of hydrocarbons.

Reaction $C_6H_6 \rightarrow C(diamond) + H_2$. A strong
shock dissociates hydrocarbons into mostly
gaseous H_2 and condensed carbon. To show
this, we made two separate CHEQ calculations
on benzene,[1] one assuming that benzene
decomposes into diamond and H_2 (in
equilibrium) and the other neglecting the
decomposition. The former gave good agreement
with experimental (P,V) data above 20GPa, and
the latter slightly below 20GPa. This
indicates that the dissociated hydrocarbon may
be in equilibrium. This is not the case for
the T deduced from the luminosity data (Fig.
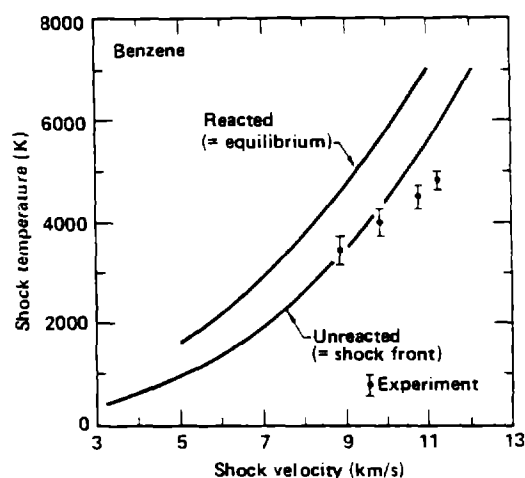4). The experimental data lie close to the

FIGURE 4
Shock temperatures of reacted and unreacted benzene: experiment[1] (points) and theory (lines).

FIGURE 5
A phase diagram of N_2-H_2O-CO_2 mixtures at 0.35eV and 33 GPa. Open circle is the theoretical C-J point of PBX-9404.

calculated equilibrium T's for unreacted benzene. This suggests that the measured T's correspond to those of the shock front prior to dissociation. An optically thick reaction zone may have prevented the radiation from the equilibrated zone from reaching the front side of the shock.

Supercritical fluid phase separations. It is well known that liquids such as water and oil do not mix well with each other. A similar "demixing" occurs in gas mixtures above their critical temperatures. A recent experiment[13] on H_2-He mixtures shows that the supercritical fluid phase separation extends to at least 7.5GPa and 350K. At such a high P and T, the molecular interactions are almost totally repulsive. Therefore, molecular arrangements which reduce repulsion can produce phase separation.

Figure 5 shows a theoretical solubility diagram for a ternary system of N_2, CO_2, and H_2O at 33GPa and 0.35eV, a state near the theoretical Chapman-Jouguet (C-J) point of PBX-9404 (open circle). We note that CO_2
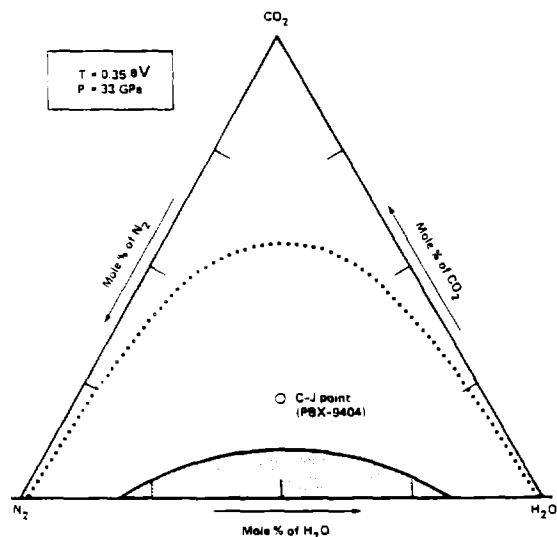
tends to make N_2 more soluble in water, in much the same way that soap makes oil and water more miscible. The shaded area represents the fluid phase separation, using Eq. (5) for the unlike-pair exp-6 parameters. However, the uncertainties in these values are about 5%. Moreover, small changes in these parameters can have large effects on the solubility boundary. For example, we can expand the mixed-phase region (area under dotted line) far beyond the C-J point simply by changing the r^* parameters for N_2-H_2O and H_2O-CO_2 by +3% and -3.5%, respectively. Therefore, we must be able to extract very accurate unlike-pair potentials from experimental solubility data.

Multicomponent systems - explosives. We assume that the detonation products are in two gaseous phases and one solid phase,i.e.,

Gas phase A: N_2, H_2O, CO_2, CO, CH_4, NH_3, H_2, O_2, NO

Gas phase B: N_2, H_2O

Solid Phase: diamond, graphite

The "three-phase" CHEQ result in Fig. 6
agrees with experiment[14] to about 60 GPa.
This is remarkable, since the two-phase
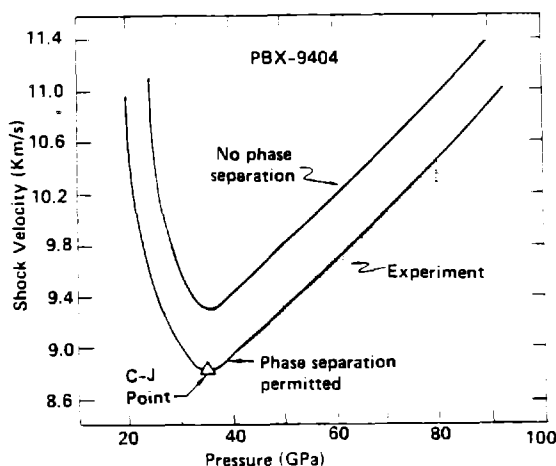calculation without phase B yields a poor
result (Fig. 6).

FIGURE 6
Hugoniots of PBX-9404: comparison between
experiment[14] (uncertainties in the shaded
area) and theory. See the text.

Carbon effect behind the detonation front.

The detonation products of HE's such as TNT
produce large amounts of condensed carbon.
Since the solidification of carbon during
detonation may be a slow process, we examined
a possible relationship between the detonation
velocity (D_{CJ}) and initial density (ρ_0) of
three HE's (PETN, RDX, and TNT) (Fig. 7). For
PETN with the smallest carbon content, we note
a decrease in slope (indicated by the arrow),
where carbon atoms in gaseous detonation
products directly condense into the diamond
phase. The equilibrium result agrees closely
with experiment. The curve for RDX, which has
a larger carbon content, shows two breaks
(arrows), the low-P break corresponding to
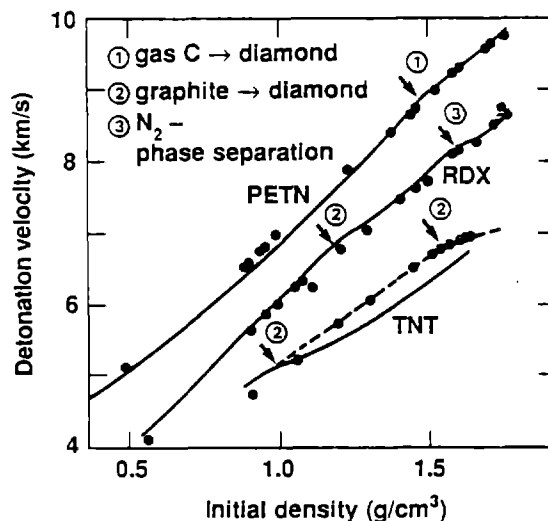diamond formation from graphitic clusters and

FIGURE 7
Detonation velocity vs. initial density. The
PETN curve is shifted upward by 1.5 km/s. See
the text. The experimental sources are in
Refs. 3, 4 and 14.

the high-P break related to the separation of
the N_2-rich fluid phase. If the solid carbon
is in its equilibrium form, the experimental
data of TNT should follow the lower curve,
which shows a change in slope at low density
due to the graphite-to-diamond transfor-
mation. In contrast, the experimental curve
changes its slope near the high-ρ_0 end in
Fig. 7. We can simulate this nonequilibrium
situation by artificially increasing the
formation energy of diamond to that of an
imperfect diamond. Our preliminary attempt in
this direction is shown by the dashed curve in
Fig. 7.

This nonequilibrium effect can be qualita-
tively explained by computing the energies of
graphite and diamond clusters, each in the
shape of a cube with n atoms along each side.
Using the standard values of the C-C and C=C
bond strengths, we can show that a graphite
cluster with $n \lesssim 10$ is stable with respect to
a diamond cluster, even if the diamond cluster

has a lower energy for a larger n.

The above conclusion is consistent with a static experiment of Hirano et al.[15] They showed that, at 9GPa, diamond forms from glassy carbon through an intermediate graphitic phase. By fitting their data to simple rate expressions, we can estimate the time necessary for the formation of graphitic and diamond clusters at different temperatures. For example, at 4000K, 5% of the initial glassy carbon sample is left after 4×10^{-6}s, and 190s later it is converted to 95 mole % of diamond. Because the pressure dependence of the activation free energy is not taken into account in the estimation process, these times are much longer than the time scale of dynamic experiments. We need similar data at different pressures to reliably estimate the rate constants.

4. SUMMARY

Our analysis shows that simple (hydrogen, nitrogen, and benzene) and complex (HE) molecules will undergo shock dissociation, and that a fluid-phase separation in the N_2-H_2O mixture is, at least, a possible explanation of differences in calculated and experimental detonation velocities. However, we need solubility experiments to further explore this. We predict that carbon microclusters in detonation products will form in a graphitic phase rather than in a diamond phase which is thermodynamically more stable. The estimated time for shock dissociation of nitrogen is consistent with available experimental evidence.

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